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rate of decomposition of smectite structure increase in the same order as the octahedral Fe and Mg substitution for Al:TR>CH>CR.

## **DETERMINATION OF VANADYL ION CONCENTRATION IN CLAY BY ELECTRON SPIN RESONANCE**

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Dielectric differences between clays and standard samples usually create discrepancies in the analysis of vanadyl ions by the ESR method. We have developed a simple method for performing a quantitative determination of vanadyl ions, using ESR data, which eliminates the above discrepancies due to varying degrees of dielectricity. Several concentrations of vanadyl standard in glycerol/kaolinite (KGa-1) mixture were prepared. The concentrations ranged from 100 to 1000 ppm. The anisotropic ESR spectra were then recorded at room temperature and integrated areas of the line (attributed to nuclear spin  $m_I = -5/2$  ||) were measured. For the vanadyl concentrations in clay lower than 120 ppm it is necessary to prepare secondary standards by mixing clay with known vanadyl content (FBT2) and clay (GB1) containing no vanadyl.

## **REPLACEMENT OF SILICON BY BORON IN THE TETRAHEDRAL POSITIONS OF PHYLLOSILICATE STRUCTURES**

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The replacement of silicon by boron in the rock-forming silicates varies over a wide range. The most important minerals are the phyllosilicates with contents up to a thousand ppm B<sub>2</sub>O<sub>3</sub> and however sometimes inosilicates for instance pyroxenes. The charge and size of the boron

atoms makes possible the replacement of aluminum or silicon atoms in the tetrahedral positions.

HARDER (1959) has shown that in the silicate muscovite, var. sericite, depending on the occurrences, a boron content up to one percent is not uncommon. FOORD et al. (1991) reported about a fine grained hard, porcellanous substance, which was subsequently identified as a mica („boromuscovite") with approximately 7.0 wt% B<sub>2</sub>O<sub>3</sub>.

The chemical analysis of a dioctahedral mica in direct contact to an olenite with excess boron (ERTL et al., 1997) from the Koralpe, Styria, exhibit a content of 3.83 wt% B<sub>2</sub>O<sub>3</sub> (ERTL & BRANDSTÄTTER, 1998). The size of the colourless, transparent crystals up to 10x10x1 mm<sup>3</sup> „invited" to single crystal X-ray work. Crystal data: a = 5.151(5), b = 8.936(4), c = 19.975(9) [Å]; β = 95.68(9) [°]; space group: C<sub>2h</sub><sup>6</sup>-C2/c.

X-ray data were collected on a STOE AED2 diffractometer with MoKα radiation, intensity calculations performed with the program system SHELXL-93. The results indicate, that the boron atoms are doubtless situated at the tetrahedral positions replacing silicon and/or aluminum. These investigations confirm for the first time the positions of boron atoms in a phyllosilicate structure by single crystal X-ray work. The conclusion that this feature can be enlarged to the whole phyllosilicates is worth to be discussed.

#### References

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## PHASE CHANGES ON HEATING HIGH-ALUMINA CLAYS

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The high alumina gibbsite/kaolinite clays are extensively used in Brazil, for the manufacture of refractories; Wefers and Misral present two sequences for the thermal transformation of synthetic gibbsite. The kaolinite sequence is well known from Brindley and Nakahira<sup>2</sup> studies. The aim of the present communication is to describe the thermal transformation of the natural gibbsite crystals in the presence of kaolinite in two Brazilian gibbsite clays with different kaolinite contents. The study of the different phases formed was conducted by transmission electron microscopy (TEM), selected area electron diffraction (SAED) and X-ray powder diffraction (XRD).